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Wide line N. M. R. investigation of solid acenapthenequinone

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Broad line NMR spectra of solid acenaphthenequinone were recorded in the temperature range 77°*K*–430°K. The comparison of the theoretical and experimental data show that the lattice is effectively rigid at the temperature 77°K. Near about room temperature the value of proton second moment shows a sudden fall. Beyond room temperature (295°K) an unusual phenomenon is observed as the second moment begins to show a definite increase. These changes were attributed to the intramolecular reorientation and canges in the crystal structure of the sample.

1. INTRODUCTION

The NMR technique has become an indispensable tool for studying crystal and molecular structure and also the intra and inter-molecular interactions. The present study reports the results of the investigations carried out on solid acenapthenequinone. Unlike those of other *P*-quinones the two $C=O$ groups in acenapthenequinone are not directly conjugated with the aromatic ring. Therefore it will be more interesting to study the phase transition and other temperature variation studies of this compound.

2. CRYSTAL AND MOLECULAR STRUCTURE

Mark & Trotter (1963) have reported the crystal structure of acenapthenequinone molecule has been shown (figure 1) to be planar within the limits of experimental error. The molecular dimensions and inter-molecular distances are normal for this type of structure. All the inter-molecular distances correspond to normal vander waals interactions. The positional coordinances of the hydrogen atoms have been shown in the following table.

	X	*Y*
H_3	0.658	0 013
H_4	0 364	0.006
H_5	0.161	0 073
H_6	0.111	0.163
H_7	0 237	0 236
H_8	0 517	0.240

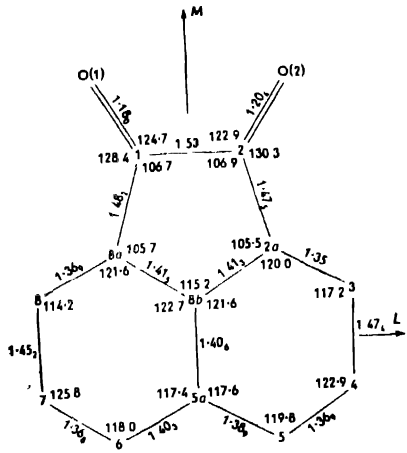

Fig. 1

. Experimental Details

The NMR experiments on solid acenapthenequinone were performed in the temperature range from 77°K to its melting points (547°K). The NMR spectrograms were recorded at the Tata Institute of Fundamental Research, Bombay, using a Varian Associates' variable frequency spectrometer on *V*-4340 variable temperature NMR probe assembly and a 12″ magnet system. The resonance frequency used was 7.5 MHZ The temperature variations were obtained by a regulated flow of heated or cooled nitrogen gas over the sample. The lowest temperature,77°K, was obtained by immersing the sample, encapsulated in a small tube, in a Dewar Flask containing liquid nitrogen.

4. Results

The experimental values of second moment were calculated with the help of the expression :

$$S = \frac{1}{3}\left[\int_0^\infty g'(H)(H-H_0)^3 dH \Big/ \int_0^\infty g'(H)(H-H_0)dH\right] - \frac{1}{4}h_m^2, \qquad \ldots \quad (1)$$

where H_0 is the resonance field strength and h_m is the amplitude of the sinusoidal field modulation (Anderew 1953).

This expression can be reduced to a simpler form by making use of the trapezium rule. The reduced form is

$$S = \frac{\Sigma h^3 f(h)}{3\Sigma h f(h)} - \frac{1}{4}h^2 m \qquad \ldots (2)$$

The experimental value of second moment thus calculated came out to be 10.71 gauss^2 at 77°K.

Intra and Inter-molecular contribution to the second moment

The intra-molecular contribution S_1 can be calculated from Van Vlecks (1948) theory The simplified expression used for this purpose is

$$S_1 = \frac{715\,9}{N} \sum_{j>k} r_{jk}^{-6} \qquad \ldots (3)$$

where N is the number of magnetic nuclei considered and r_{jk} is the distance between the j-th and the k-th nuclei. The substitution of the various values yielded $S_1 = 3\,71$ gauss^2. The method of calculating the accurate intermolecular second moment S_2 is very tedious. A rough extimate of S_2 may be obtained by an approximate formula (Smith 1965).

$$S_2 = 358\,1 \times 4\pi N_p (3R^3 V)^{-1} \qquad \ldots (4)$$

where N_p is the number of protons per unit cell. R is the molecular radius and V is the unit cell volume in cubic angstroms. The substitution of the values of $V = 812$Å^3, $N_p = 24$ and $R = 1.92$Å in eq (4) yields $S_2 = 6.27$ gauss^2 for the sample under investigation.

The total rigid lattice second moment thus comes out to be $3.72+6.27 = 9.99$ gauss^2. This value compares favourably with the calculated value 10.71 gauss^2 at 77°K.

5. Discussion

In the present NMR investigation of acenapthenequinone, the experimental second moment value at 77°K is found to be 10.71 gauss^2 (figure 2). This value

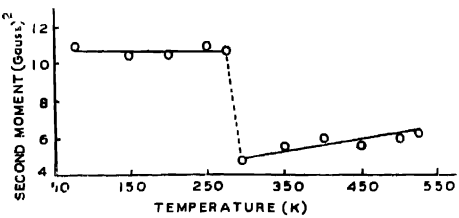

Fig. 2

agrees well with the theoretically calculated value of 9.99 gauss^2 showing that at this temperature the lattice is static and devoid of any motion whatsoever. As the temperature of the sample is increased gradually, the value of the proton second moment remains constant until near about room temperature, it drops suddenly to 4.85 gauss^2 The above reduction in the value of the proton second moment may be attributed to the concurrance of molecular reorientation in solid acenaphthenequinone The effect of molecular motion on second moment was calculated using the method first suggested by Gutowsky & Pake (1950). For a poly-crystalline sample in which the molecular reorientation occurs about the n fold symmetry axis, the intra-molecular contribution to the observable spectrum is reduced by a factor

$$F = \frac{1}{4}(3\cos^2 r_{jk} - 1)$$

where r_{jk} is the angle between the internuclear vector considered and the reorientation axis A rough value of second moment for general molecular reorientation about the centre of gravity can be obtained by the replacement of r by the centre to centre molecular separation in Van Vleck expression for intra-molecular contribution to the second moment, i.e. by concentrating all the nuclei at their molecular centres Andrew & Eades (1953) observed that the rotation of the molecule about the corresponding axis reduces the inter molecular contribution to the second moment by a factor 0 24 This gives a value of 1 50 gauss^2 for intermolecular contribution when the rotation of the molecule sets in. However, an accurate evaluation of intramolecular contribution is difficult, roughly it has been estimated adopting Gutowsky and Pake method to be about 2.72 gauss^2. The total value of the reduced second moment thus comes out to be $2.72 + 1\ 50 = 4.22$ gauss^2 This value compares favourable with the experimentally measured value of the second moment (4.85 ± 1 gauss^2) at 295°K

As the temperature of the sample is increased beyond the room temperature an unusual phenomenon is observed The proton second moment shows a gradual increase until near about the melting point it attains a value about 6.5 gauss^2 These changes can be attributed to the change in the crystal structure of the sample beyond 295°K The intra-molecular reorientation is responsible only for the decrease in the value of the second moment at temperatures much lower than the melting point. At higher temperatures, the changes in the crystal structure play a more prominent role and thus mars the effect of intra-molecular contribution thereby increasing the value of the second moment and consequently the second moment Vs temperature Curve shows an unusual negative slope at temperature considerably higher than room temperature.

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